Supplemental Material

For

Direct Detection of Products from the Pyrolysis of 2-Phenethyl Phenyl Ether

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This supplemental material contains Cartesian coordinates (Angstroms) for all structures at the CBS-QB3 level of theory.

2-Phenethyl phenyl ether (PPE, **1**)

Atom	X	Y	Z
C	-0.000089	0.000001	0.000134
H	-0.000033	0.000127	1.093657
H	1.044624	-0.000151	-0.321934
C	-0.652749	-1.295363	-0.479695
H	-1.699113	-1.341369	-0.153452
H	-0.634373	-1.350112	-1.575176
O	0.087303	-2.377030	0.082425
C	-0.716977	1.221883	-0.529508
C	-1.828493	1.744616	0.140775
C	-0.306434	1.838113	-1.716171
C	-2.511717	2.850160	-0.359723
H	-2.155476	1.286012	1.068919
C	-0.986502	2.944518	-2.220515
H	0.558891	1.451757	-2.245700
C	-2.092639	3.453377	-1.543824
H	-3.367451	3.243832	0.177556
H	-0.649321	3.411607	-3.139265
H	-2.620822	4.316387	-1.933149
C	-0.297489	-3.657343	-0.193986
C	0.473813	-4.665002	0.399041
C	-1.380483	-4.002096	-1.007327
C	0.163282	-5.999142	0.179454
H	1.308236	-4.372677	1.025075
C	-1.680054	-5.349715	-1.218547
H	-1.989802	-3.241240	-1.476021
C	-0.917449	-6.352570	-0.632042
H	0.768290	-6.769613	0.644577
H	-2.522461	-5.607838	-1.850917
H	-1.158053	-7.395299	-0.801681

2-phenylethyl radical (**2**)

Atom	X	Y	Z

Phenoxy radical, C_{2V} (**3**)

Atom	X	Y	Z

C	0.000000	0.000000	1.048535
C	0.000000	0.000000	-1.782051
C	0.000000	1.237795	0.288957
C	0.000000	-1.237795	0.288957
C	0.000000	-1.223634	-1.085662
C	0.000000	1.223634	-1.085662
O	0.000000	0.000000	2.299995
H	0.000000	0.000000	-2.866013
H	0.000000	2.160862	0.856607
H	0.000000	-2.160862	0.856607
H	0.000000	-2.153887	-1.642799
H	0.000000	2.153887	-1.642799

Benzyl radical, C_{2V} (**4**)

Atom	X	Y	Z
C	0.000000	1.216482	0.251222
C	0.000000	1.209811	-1.131562
C	0.000000	0.000000	-1.836275
C	0.000000	-1.209811	-1.131562
C	0.000000	-1.216482	0.251222
C	0.000000	0.000000	0.994121
C	0.000000	0.000000	2.398056
H	0.000000	2.157588	0.790897
H	0.000000	2.149014	-1.673968
H	0.000000	0.000000	-2.919995
H	0.000000	-2.149014	-1.673968
H	0.000000	-2.157588	0.790897
H	0.000000	-0.927127	2.957403
H	0.000000	0.927127	2.957403

anisyl radical (**5**)

Atom	X	Y	Z
C	-2.010828	-0.047157	-1.013152
C	-2.007340	-0.045974	0.382779
C	-0.808120	-0.052265	1.083851
C	0.399636	-0.059344	0.383591
C	0.411493	-0.074205	-1.011320
C	-0.800738	-0.064279	-1.700496
H	-2.947977	-0.040851	-1.556949
H	-2.943797	-0.037222	0.928944

H	-0.782069	-0.047307	2.166629
H	1.349518	-0.120695	-1.548907
H	-0.792217	-0.079917	-2.784610
O	1.541258	-0.080149	1.151343
C	2.733019	0.296023	0.613030
H	2.730806	1.063805	-0.152623
H	3.552943	0.186580	1.307083

6-centered transition state (Hoffmann, **6**)

Atom	X	Y	Z
C	0.000000	0.000000	0.000000
C	0.000000	0.000000	1.451162
O	1.112924	0.000000	2.068751
C	2.064861	-1.788779	1.583365
C	1.744590	-2.119474	0.262898
C	2.681850	-1.837787	-0.859657
C	2.737145	-2.696991	-1.964237
C	-1.248258	-0.065367	-0.708879
H	0.832463	0.505077	-0.486186
H	1.559594	-2.280201	2.402423
H	2.996359	-1.301187	1.829605
H	0.695992	-1.198625	0.003560
H	1.114580	-2.998053	0.128074
H	2.104027	-3.578352	-1.985317
C	3.600426	-2.441814	-3.026048
C	-2.421562	-0.246009	-0.031486
H	-1.244544	0.025794	-1.789854
H	-3.361962	-0.314980	-0.565889
C	-2.418060	-0.307496	1.391171
C	-1.256020	-0.212336	2.111225
H	-3.362218	-0.431073	1.912136
H	-1.251459	-0.256997	3.194407
C	4.420772	-1.315709	-3.008009
H	3.633570	-3.124784	-3.867791
H	5.093513	-1.115900	-3.834176
C	4.364851	-0.445071	-1.920998
C	3.501117	-0.699254	-0.859417
H	4.991967	0.439466	-1.901100
H	3.453044	-0.005439	-0.026865

Styrene, C_S (**7**)

Atom	X	Y	Z
C	0.680246	0.000000	0.852473

C	1.892088	0.000000	0.174380
C	1.921144	0.000000	-1.221292
C	0.723708	0.000000	-1.930790
C	-0.490118	0.000000	-1.249259
C	-0.537947	0.000000	0.152714
C	-1.849929	0.000000	0.819678
C	-2.098324	0.000000	2.131610
H	0.680353	0.000000	1.936221
H	2.820540	0.000000	0.734762
H	2.869007	0.000000	-1.747396
H	0.733100	0.000000	-3.015093
H	-1.420270	0.000000	-1.808453
H	-2.699658	0.000000	0.140225
H	-3.115599	0.000000	2.503854
H	-1.312678	0.000000	2.878802

2,4-cyclohexadienone (**8**)

Atom	X	Y	Z
O	-2.302345	0.003874	-0.000136
C	-0.317188	1.278785	0.000087
C	1.032472	1.276395	0.000021
C	1.815313	0.048292	-0.000081
C	1.211925	-1.148841	-0.000046
C	-0.279544	-1.277106	0.000122
C	-1.084741	0.025660	0.000011
H	-0.893398	2.196787	0.000132
H	1.569677	2.220149	0.000025
H	2.896647	0.124503	-0.000186
H	1.797145	-2.063165	-0.000117
H	-0.610476	-1.864345	-0.866543
H	-0.610257	-1.864034	0.867088

4-centered transition state (Maccoll, **9**)

Atom	X	Y	Z
C	-0.549240	-0.131923	0.194462
H	-0.560948	-0.008368	1.500812
H	0.458509	-0.445736	-0.069175
C	-1.440213	-1.164144	0.555577
H	-2.513224	-1.044549	0.483553
H	-1.077008	-2.164063	0.757567
O	-1.350560	-0.533976	2.505649

C	-1.024794	1.134910	-0.432512
C	-2.182158	1.782763	0.022217
C	-0.305166	1.712315	-1.484995
C	-2.618103	2.959402	-0.578557
H	-2.722471	1.376972	0.870924
C	-0.739062	2.893301	-2.081874
H	0.597116	1.227569	-1.843713
C	-1.900450	3.518796	-1.634889
H	-3.513675	3.448383	-0.211586
H	-0.170028	3.322979	-2.898879
H	-2.238679	4.438442	-2.098433
C	-0.990044	-1.242098	3.590165
C	-1.814532	-2.273878	4.072168
C	0.218887	-0.974924	4.256629
C	-1.430827	-3.019104	5.181583
H	-2.753842	-2.469280	3.567091
C	0.582979	-1.719396	5.374022
H	0.847259	-0.167439	3.897620
C	-0.232238	-2.749019	5.842067
H	-2.078044	-3.813753	5.537731
H	1.515251	-1.493707	5.881022
H	0.058360	-3.327693	6.710892

Phenol (**10**)

Atom	X	Y	Z
C	-1.567382	0.134128	-0.982733
C	-1.610523	0.126658	0.412062
C	-0.442444	0.026538	1.158752
C	0.789302	-0.067659	0.506837
C	0.841651	-0.060874	-0.888464
C	-0.336421	0.039857	-1.625925
H	-2.481533	0.212398	-1.558830
H	-2.563133	0.199464	0.924988
H	-0.460969	0.019543	2.241821
H	1.799649	-0.134075	-1.395689
H	-0.285905	0.044323	-2.709055
O	1.907855	-0.163949	1.286684
H	2.683946	-0.221955	0.720126

ethyl vinyl ether (**11**)

Atom	X	Y	Z
O	-0.051375	0.293411	0.077424
C	0.196859	-0.997585	0.643607
C	0.207375	-0.851399	2.152403
C	-0.097056	0.349199	-1.280009
C	-0.314054	1.480049	-1.945701
H	1.160627	-1.379144	0.282500
H	-0.587508	-1.696433	0.325427
H	0.394784	-1.818921	2.625253
H	0.988627	-0.154916	2.463900
H	-0.753089	-0.471334	2.506721
H	0.056132	-0.598915	-1.793199
H	-0.342169	1.473266	-3.026167
H	-0.465142	2.417521	-1.425632

TS Reaction 5 (**12**)

Atom	X	Y	Z
O	0.475501	-1.209345	-0.215142
C	-1.478676	-0.520271	-0.042411
C	-1.413681	0.869686	0.134583
C	1.247907	-0.349902	0.294952
C	1.346191	0.949931	-0.206559
H	-1.615324	-1.185541	0.798001
H	-1.677767	-0.947736	-1.013960
H	-1.756399	1.491755	-0.689540
H	-1.666568	1.259955	1.118572
H	-0.130444	1.125086	0.110262
H	1.692601	-0.555191	1.285172
H	1.152342	1.118762	-1.261008
H	1.987108	1.671008	0.290254

Diethyl ether, C_{2V} (**13**)

Atom	X	Y	Z
O	0.000000	0.000000	0.254648
C	0.000000	1.185535	-0.522368
C	0.000000	-1.185535	-0.522368
C	0.000000	2.377559	0.416892
C	0.000000	-2.377559	0.416892
H	0.886497	1.208556	-1.176085
H	-0.886497	1.208556	-1.176085
H	0.886497	-1.208556	-1.176085
H	-0.886497	-1.208556	-1.176085
H	0.000000	3.313557	-0.148163
H	0.000000	-3.313557	-0.148163
H	-0.884810	2.358495	1.057298
H	0.884810	2.358495	1.057298
H	0.884810	-2.358495	1.057298
H	-0.884810	-2.358495	1.057298

TS Reaction 6 (**14**)

Atom	X	Y	Z
O	-0.059033	0.118959	-0.508614
C	1.703317	0.634393	-0.020846
C	-1.157282	0.431255	0.333751
C	2.110819	-0.708805	0.163828
C	-2.377149	-0.401766	-0.044816
H	1.915661	1.167752	-0.939036
H	1.458620	1.264667	0.828369
H	-1.389983	1.497273	0.223401
H	-0.896692	0.257440	1.391881
H	2.273674	-1.058675	1.177975
H	-3.235034	-0.139661	0.582433
H	0.749445	-0.806949	-0.183886
H	2.733716	-1.166858	-0.596900
H	-2.643590	-0.229569	-1.089994
H	-2.171782	-1.467554	0.083169

Phenyl ethyl ether (PEE, **15**)

Atom	X	Y	Z

C	-2.374274	-1.235509	-0.920070
C	-2.372961	0.161540	-0.919225
C	-1.258755	0.865871	-0.487368
C	-0.119871	0.179304	-0.046289
C	-0.113351	-1.218487	-0.044110
C	-1.243052	-1.913189	-0.481958
H	-3.246011	-1.783083	-1.257946
H	-3.247707	0.705667	-1.258014
H	-1.240541	1.949015	-0.480056
H	0.753499	-1.771136	0.291607
H	-1.227892	-2.997594	-0.476341
O	0.922530	0.960887	0.357792
C	2.119995	0.335614	0.821116
H	1.896426	-0.300999	1.686378
H	2.537589	-0.300148	0.030319
C	3.092397	1.436953	1.198177
H	4.028973	1.005090	1.560357
H	3.311948	2.067293	0.333993
H	2.672717	2.066217	1.985733

TS Reaction 8 (Hoffmann, **16**), CBS-QB3 (0 K)= -385.290610 hartree

Atom	X	Y	Z
C	-0.049955	-0.035538	0.033674
C	-0.009135	-0.124842	1.395922
C	1.250629	-0.148227	2.086700
C	2.490700	-0.231633	1.328682
C	2.385838	-0.106684	-0.102933
C	1.164216	-0.034689	-0.714612
H	-0.998484	0.006983	-0.488904
H	-0.927642	-0.169978	1.971779
H	1.277981	-0.565548	3.090365
H	3.308636	-0.118544	-0.671849
H	1.109790	0.018945	-1.797480
O	3.595990	-0.234981	1.939654
C	3.692973	1.690757	2.996334
H	4.183559	1.153221	3.794530
H	4.325501	2.009890	2.180768
C	2.389486	2.145725	3.125266
H	2.053362	2.954836	2.481298
H	1.637295	1.121894	2.543602
H	1.927377	2.119728	4.108998

TS Reaction 9 (Maccoll, **17**), CBS-QB3 (0 K)= -385.277507 hartree

Atom	X	Y	Z
C	-0.000676	0.000807	0.000579
C	-0.001436	0.006477	1.395734
C	1.192576	0.006058	2.107629
C	2.425636	-0.016325	1.430356
C	2.421061	-0.023788	0.023265
C	1.218315	-0.008236	-0.675774
H	-0.934281	0.009900	-0.549414
H	-0.942201	0.019649	1.936265
H	1.195789	0.027688	3.191696
H	3.369108	-0.019769	-0.503224
H	1.235591	-0.006002	-1.760681
O	3.576693	-0.037826	2.118090
C	4.406253	-1.602510	3.214337
H	4.413275	-1.035737	4.135712
H	3.568389	-2.274681	3.073629
C	5.495187	-1.587667	2.329265
H	5.579206	-2.392254	1.605426
H	4.765631	-0.646468	1.783854
H	6.429253	-1.148304	2.663990

Cyclopentadienyl radical (**18**)
Propargyl radical (**19**)
TS Reaction 13 (**20**)

Benzene (**21**)

Atom	X	Y	Z
C	1.207171	0.696960	0.000000
C	0.000000	1.393921	0.000000
C	-1.207171	0.696960	0.000000
C	-1.207171	-0.696960	0.000000
C	0.000000	-1.393921	0.000000
C	1.207171	-0.696960	0.000000
H	2.146315	1.239175	0.000000
H	0.000000	2.478351	0.000000
H	-2.146315	1.239175	0.000000
H	-2.146315	-1.239175	0.000000
H	0.000000	-2.478351	0.000000
H	2.146315	-1.239175	0.000000

Benzyloxy radical (**22**)

Atom	X	Y	Z
C	-2.264180	0.277297	0.000000
C	-1.801513	-1.037869	0.000000
C	-0.433089	-1.294255	0.000000
C	0.484740	-0.240270	0.000000
C	0.017489	1.073164	0.000000
C	-1.351780	1.330635	0.000000
H	-3.329475	0.478749	0.000000
H	-2.506136	-1.862068	0.000000
H	-0.078147	-2.321234	0.000000
H	0.736963	1.882979	0.000000
H	-1.706540	2.355378	0.000000
O	2.823184	0.525278	0.000000
C	1.974100	-0.531925	0.000000
H	2.244851	-1.177604	-0.862560
H	2.244851	-1.177604	0.862560

Benzaldehyde (**23**)

Atom	X	Y	Z
C	-1.996570	0.000000	-0.987918
C	-1.989727	0.000000	0.405755
C	-0.777207	0.000000	1.089450
C	0.428286	0.000000	0.381766
C	0.415297	0.000000	-1.019045
C	-0.793991	0.000000	-1.700070
H	-2.940026	0.000000	-1.522471
H	-2.924732	0.000000	0.954004
H	-0.761256	0.000000	2.175120
H	1.362767	0.000000	-1.544926
H	-0.807205	0.000000	-2.784028
C	1.714648	0.000000	1.116756
H	1.612700	0.000000	2.223856
O	2.806666	0.000000	0.597285

Phenyl radical, C_{2V} (**24**)

Atom	X	Y	Z
C	0.000000	0.000000	-1.321964

C	0.000000	1.211882	-0.631391
C	0.000000	1.223888	0.770629
C	0.000000	0.000000	1.395872
C	0.000000	-1.223888	0.770629
C	0.000000	-1.211882	-0.631391
H	0.000000	0.000000	-2.405930
H	0.000000	2.150423	-1.175990
H	0.000000	2.157664	1.321802
H	0.000000	-2.157664	1.321802
H	0.000000	-2.150423	-1.175990

TS Reaction 17 (**25**)

Anisole (methoxybenzene, **26**)

Atom	X	Y	Z
C	-0.886869	-2.127371	0.000000
C	-1.806323	-1.075334	0.000000
C	-1.371301	0.241776	0.000000
C	-0.000044	0.528407	0.000000
C	0.926445	-0.517790	0.000000
C	0.472435	-1.838650	0.000000
H	-1.229628	-3.155229	0.000000
H	-2.870505	-1.283928	0.000000
H	-2.069487	1.070121	0.000000
H	1.990019	-0.320758	0.000000
H	1.198530	-2.644242	0.000000
O	0.326948	1.853396	0.000000
C	1.700976	2.210819	0.000000
H	1.725340	3.299397	0.000000
H	2.214118	1.838162	0.893822
H	2.214118	1.838162	-0.893822

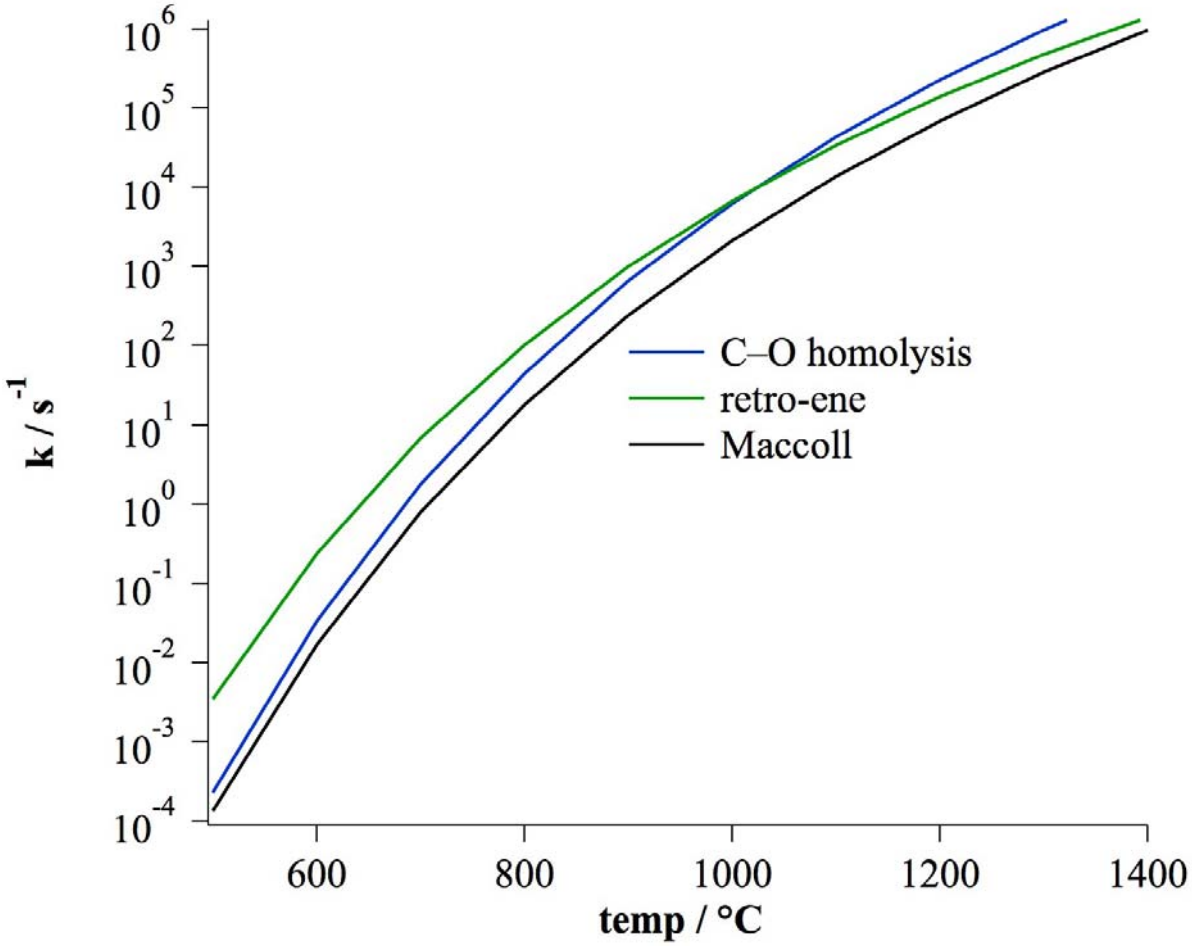

Figure S1. Kinetic rate plot for PEE. C-C reaction not considered.

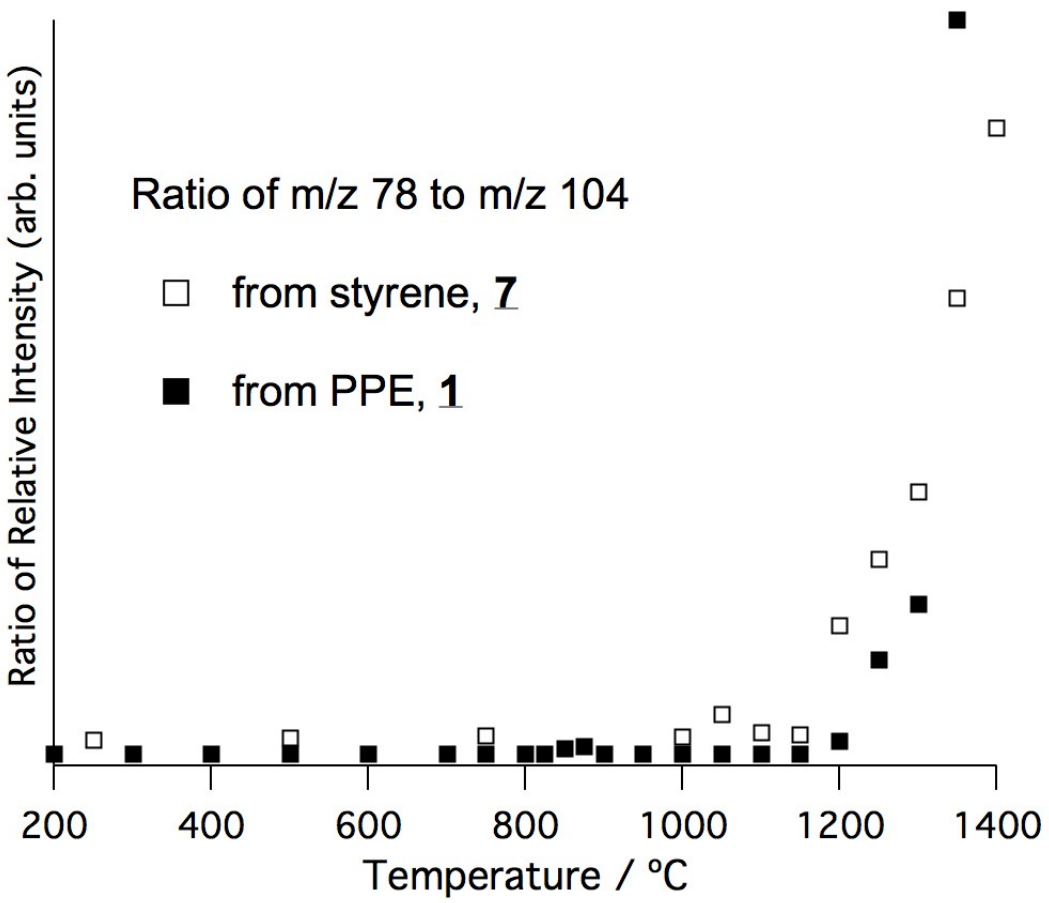

Figure S2. Comparison of m/z 78 (benzene) produced from styrene pyrolysis (open symbols) and PPE pyrolysis. The ratio of m/z 78/104 was calculated from the raw data. This suggests the m/z 78 observed in the PPE experiment was due to styrene pyrolysis only.

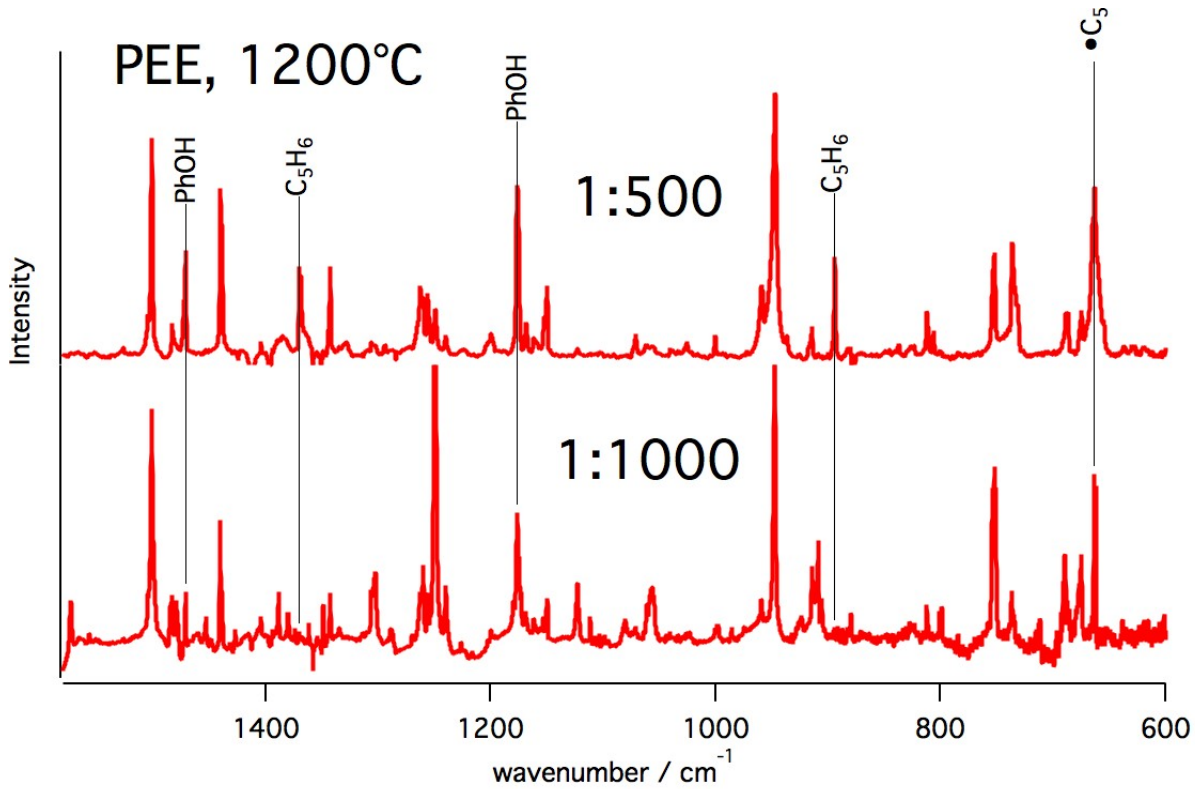

Figure S3. Matrix data from PEE pyrolysis at 1200˚C at high concentration (top, 1:500) and low concentration (bottom, 1:1000) showing that cyclopentadiene (CPD) formation is eliminated at low concentration, but phenol concentration remains constant, consistent with unimolecular production of phenol from PEE via a concerted reaction.

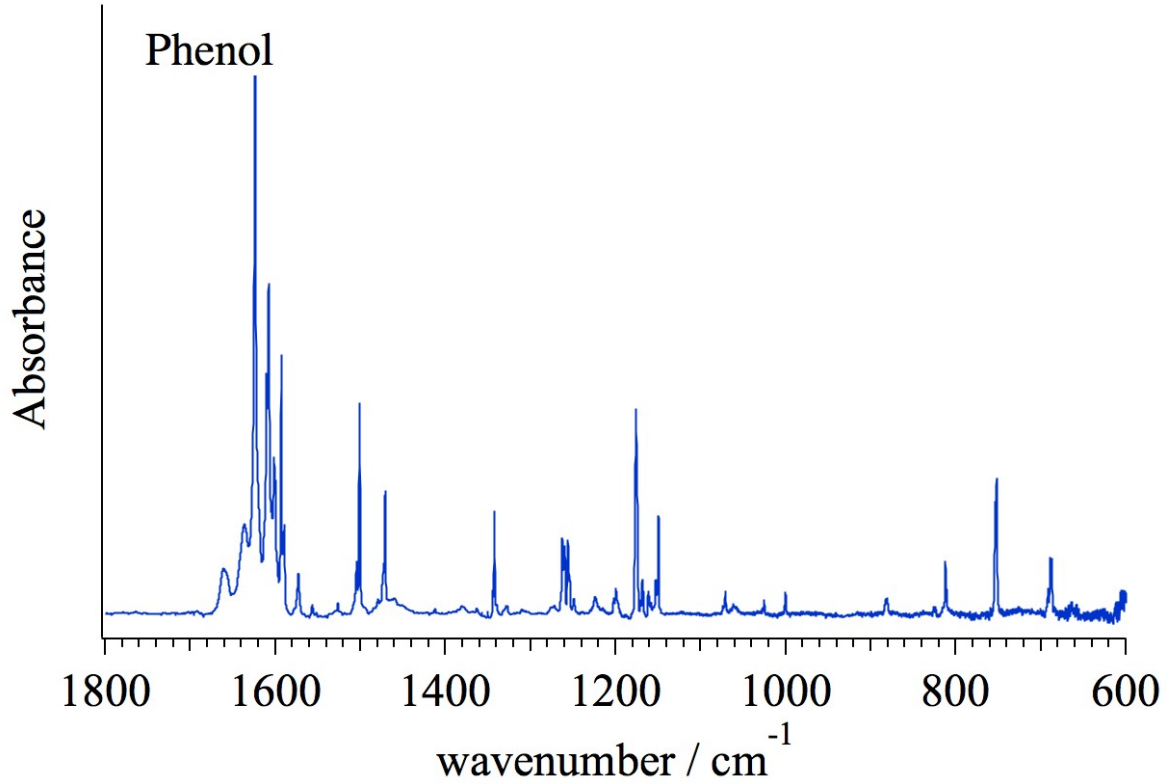

Figure S4. Matrix-IR spectra of Phenol only.

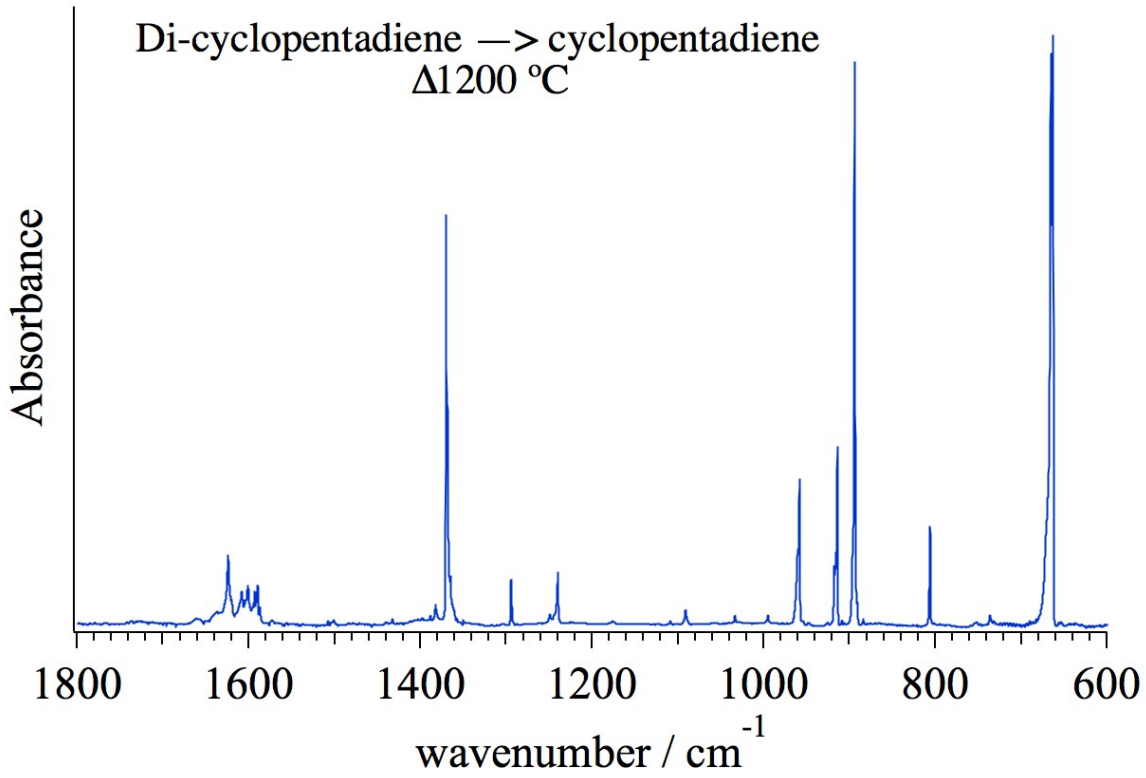

Figure S5. Matrix-IR spectra of cyclopentadiene from pyrolysis at 1200 ˚C of di-cyclopentadiene.